PART 1

INTRODUCTION

Chapter 7. Hindcasting and Forecasting Functions for PCBs in the Lake Michigan Ecosystem

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1.7.1 Introduction

The challenge for both hindcasting and forecasting is the development of functions that represent the change of polychlorinated biphenyl (PCB) loads to the lake with time. To accomplish this, quality historical databases are required that bracket both sides of the peak load to the lake. The use of PCB production information are of limited usefulness. They do not represent the historical use of PCBs in the Lake Michigan basin. The early use of PCBs was primarily in sealed containers as capacitors and transformers. PCBs were not released except at points of manufacture and locations where capacitors and transformers were manufactured. The number of these sites was limited. None were within the Lake Michigan basin. The open use of PCBs within the basin were primarily for the manufacture of carbonless paper and as a hydraulic fluid for die-casting. The first recorded use of PCBs for manufacture of carbonless paper was in 1954 in the Fox River Valley at Green Bay, Wisconsin (Table 1.7.1). In the Fox River Valley, its use for this purpose peaked in 1969-1970. Its use for production of the paper as well as recycling of the paper was phased out in 1971-1972. Other locations associated with production of this carbonless paper or its recycling included the Manistique and Kalamazoo Rivers. The use of hydraulic fluids with PCBs began in 1948 and ended in 1971 at Waukegan, Illinois. Another location where these hydraulic fluids were used was Sheboygan, Wisconsin. It appears that these two uses are most responsible for the loads of PCBs to Lake Michigan. These uses are poorly quantified. Therefore, historical observations of PCBs in various media were used to construct load functions for both forecasts and hindcasts.

1.7.2 Forecast Functions

Functions developed for the purpose of forecasting PCBs in various media were developed from the 1994-1995 Lake Michigan Mass Balance Project (LMMBP) data and data from various published and unpublished sources. The data were used to develop functions that describe the apparent loading trends for PCB loads from the atmosphere and tributaries. Data were extremely limited. Historical data are of unknown quality due to changes in methodology. Specifically, those data generated using packed columns rather than capillary columns for the gas chromatography are suspect. Packed columns did not provide a good separation of PCB peaks. Older results were expressed as Aroclors rather than congeners. These weaknesses can lead to a high bias. However, these data were all that

Table 1.7.1. Significant Dates in the History of PCBs in the Lake Michigan Basin

Date	Event
1865	First PCB-like chemical discovered
1881	First PCBs synthesized
1914	Measurable amounts of PCBs found in bird feathers
1927	PCBs first manufactured at Anniston, Alabama
1935	PCBs manufactured at Anniston, Alabama and Sauget, Illinois
1948-1971	Outboard Marine Corporation at Waukegan, Illinois purchased eight million gallons of hydraulic fluid with PCBs
1954	Appleton Paper Company began using PCBs as PCB-coated carbonless copy paper
Mid-1950s to Mid-1960s	PCBs loaded to Kalamazoo River from deinking
1950s to 1980s	PCBs discharged to Manistique River and Harbor
1959-1972	Outboard Marine Corporation at Waukegan, Illinois used hydraulic fluid with PCBs for die-casting
1959-1971	PCBs used by Tecumseh Products Company as a hydraulic fluid was loaded to Sheboygan River
1969-1970	Paper company discharges of PCBs to Fox River peaked
1970	PCB production peaked at 85 million pounds and huge contamination noted at Sauget, Illinois plant
1971-1972	Appleton Paper Company and NCR Corporation phased out PCB use. Recycling of carbonless paper had occurred for several decades
1973	U.S. Food and Drug Administration (USFDA) establish 5 ppm PCB tolerance level in fish
1975	124,000 cans of salmon from Lake Michigan seized because of PCBs
1977	PCB production ends
1984	USFDA lowered PCB tolerance level in fish to 2 ppm
1985	Commercial fishing for carp and other valuable species outlawed on Green Bay
1991	End Sheboygan River PCB remediation of upper river
1991	U.S. Department of Health and Human Services label PCBs as possible carcinogen
1992	End Waukegan Harbor PCB remediation
1998	The eight Great Lakes states agreed on a “Great Lakes Protocol for Fish Consumption Advisories” that lowered the regional standard from the USFDA commercial standard of 2 ppm down to 0.05 ppm
1997-1998	Milwaukee River PCB remediation
2001	Manistique Harbor PCB remediation completed
2002	Possibly begin Grand Calumet River PCB remediation

were available at the time of model development and execution.

1.7.2.1 Tributary Loads

Several data sets were used to develop a first-order exponential decay function for tributary loads. The derivation of the PCB loading attenuation rate half-life for tributaries is straightforward. It utilized 1994 and 1995 LMMBP tributary data (McCarty *et al.*, 2004) along with data for the Fox River for 1989-1990 (Velleux and Endicott, 1994) and for Lake Michigan tributaries for 1982 (Marti and Armstrong, 1990). The loading data for the Fox River, Lake Michigan tributaries, and 1994-1995 were fit using Equation 1.7.1.

$$C_1 = C_2 e^{-kt} \tag{1.7.1}$$

where:

C_1 = load at time t_1

C_2 = load at time t_2

k = attenuation rate

t = interval of time between t_1 and t_2

The equation was solved for k. For the Fox River and Lake Michigan tributaries, k was calculated to be 0.053/year and 0.054/year, respectively. These yielded the half-lives of 12-13 years. The k of 0.054/year was used.

Recent reports of half-lives for individual tributaries range from 6.1 years (k = 0.114/year) in the Kalamazoo River (Blasland, Bouck and Lee, Inc., 2000) to 6.8 years (k = 0.102/year) at the Fox River DePere Dam and 9.0 years (k = 0.077/year) at the river mouth (Limno Tech, Inc., 2002). Thus, the choice of a k equal to 0.054 is probably conservative for the purposes of a forecast; that is, tributary loadings could be biased high, leading to later dates when lake trout will cease to have consumption advisories.

1.7.2.2 Atmospheric Loads

For the period of 1992 to 1997, Simcik *et al*. (2000) reported a half-life of 6.9 ± 3.5 for precipitation. The half-life for atmospheric vapor phase PCBs was taken as reported by Schneider *et al*. (2001) based upon the work of Hillery *et al*. (1997). Hillery *et al*. (1997) based their work on the 1992-1995 International Atmospheric Deposition Network (IADN) data. At that time, the reported half-life was six years. This is one of the bounding half-lives used for all forecasts. More recently published half-lives include those of Simcik *et al*. (1999) who reported half-lives of 2.7 years and 3.0 years over water and land, respectively. Their results were based on 1992-1997 IADN data. For the period of 1992 through 2000 at Sleeping Bear Dunes, Buehler *et al*. (2002) reported half-lives of 3.1 ± 0.7 years for 1992 through 1995, 4.9 ± 0.9 years for 1992 through 1997, and 20.0 ± 8.6 years for 1992 through 2000. For the period of 1992 through 2001, an examination of the temperature-corrected PCB partial pressure IADN data revealed that partial pressures were declining at Sleeping Bear Dunes with a half-life rate of 8.3 ± 1.5 years (Buehler *et al*., 2004). Because of the uncertainty concerning the rate of decline and the apparent increase in half-life with the addition of more recent data, bounding half-lives of 6 and 20 years were used for the purposes of the forecasts. The uncertainty in the half-life of atmospheric vapor phase PCBs suggests that a half-life of 13 years for tributaries is within reason.

1.7.3 Hindcast Functions

Development of a hindcast load function was more problematic. The only data that exist for years prior to the year of peak load are for preserved museum forage fish specimens (Neidermyer and Hickey, 1976) and lake trout (DeVault *et al*., 1996). Though the forage fish data can not be used for a hindcast because they are preserved specimens, they do provide valuable information about when PCBs first appeared in Lake Michigan fish. The fourhorn sculpin data are of most interest. PCBs were not detected in the fish collected in 1949 but were found in fish collected in 1951. For rainbow smelt, PCBs were not detected in 1942 but were detected and measured in 1960. This is consistent with the first known reported purchase of hydraulic fluids with PCBs in 1948 for use at Waukegan, Illinois. Thus, it appears contamination of the lake with PCBs did not begin until after 1948. The lake trout annual data only go back to 1972 (DeVault *et al*., 1996). The peak in the lake trout occurred in 1974-1975; hence, not enough data for establishing a function for the onset of contamination.

The only way currently available to reconstruct the load function of PCBs for the lake was to utilize information available from dated sediment cores. The number of sediment cores for which data are available are limited (Figure 1.7.1). Cores SLMD, SLMF, CLMM, NLMB, and NLME are from the work of Hermanson *et al*. (1991). The 18S core is from Swackhamer and Armstrong (1988), the HMS1 core is from Schneider *et al*. (2001), and cores 18G, 47s, and 68k are from Golden *et al*. (1993). The LMMBP cores are from Stations 15, 61, and 86 (Van Hoof and Eadie, personal communication). All the cores are of varying quality. Core quality is dependent upon sedimentation rate, depth of surficial sediment mixing by physical and biological processes, location with respect to sources, and thickness of the core interval samples. Of 13 cores, core 15 is of the highest quality. Sedimentation rate (0.2235 g/cm^2/year) is one of the highest for Lake Michigan (core is highly resolved with the surficial 1 cm representing 1.2 years of deposition), its mixed layer is less than the 1 cm interval sampled, and it is located in an area of the lake that is very responsive to loadings. The location of core 15 is in the region impacted by an annual spring plume of suspended

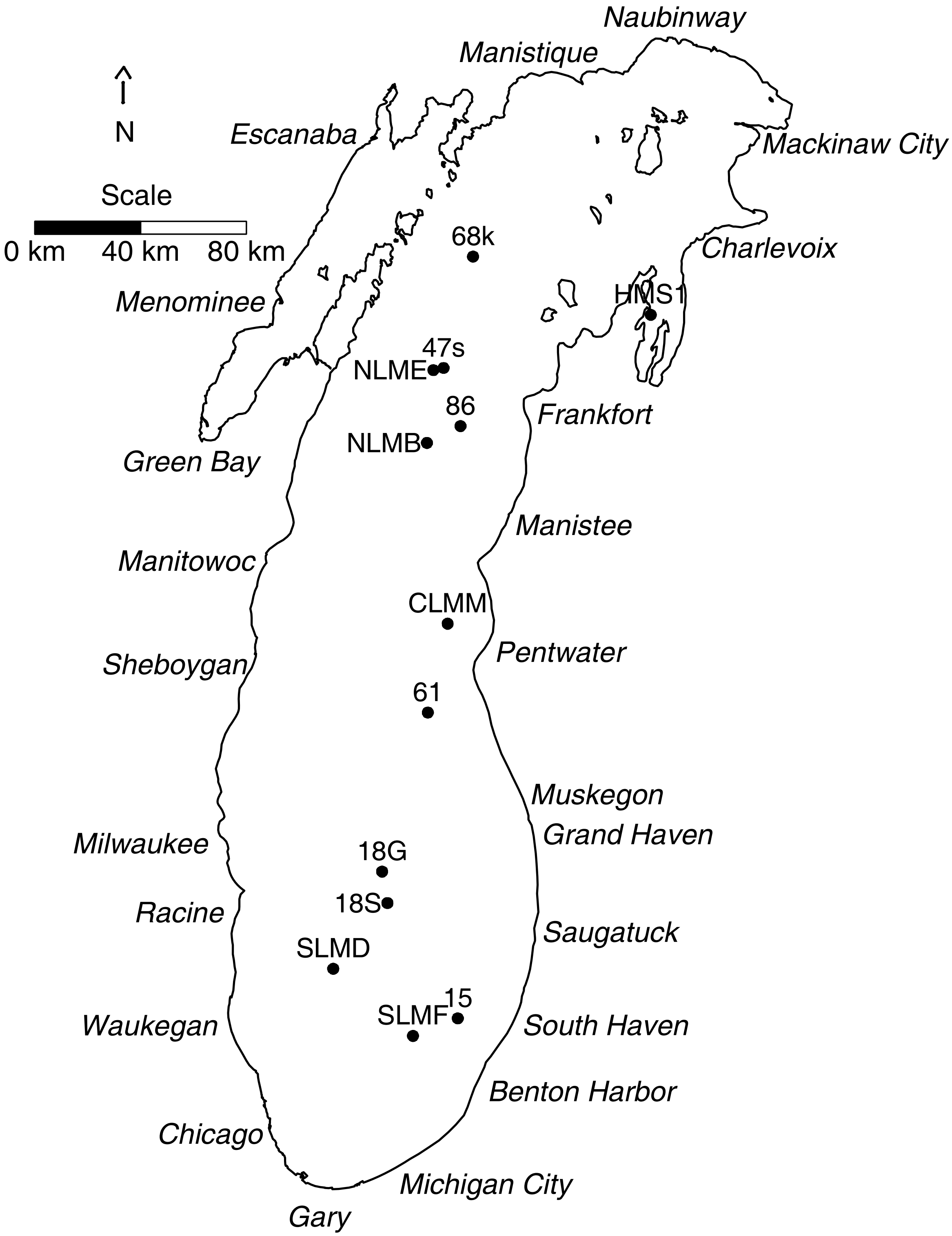

Figure 1.7.1. Locations of dated cores analyzed for PCBs by Hermanson *et al.* (1981), Swackhamer and Armstrong (1988), Schneider *et al.* (2001), Golden *et al.* (1993), and Van Hoof (personal communication) for the LMMBP.

particulate matter that has concentrations four to 10 times that of the lake (Eadie *et al.*, 1996). Because core 15 is highly resolved, relatively undisturbed by post-depositional mixing processes (mixed layer less than 1 cm), and in a region responsive to an annual transport event in the lake, it was chosen for the development of a total PCB loading function for the lake.

The distribution of PCBs within the core with time can be broken into two linear functions; one prior to peak concentration and one after peak concentration (Figure 1.7.2). The pre-peak function was based on the period of 1947 to 1965, and the post-peak function was based on the period 1972 to 1994. The two functions crossed one another in 1967, indicating this should be the peak load year. The exact location of the peak was problematic because there are two peaks in the observed data. The year of peak loading was constrained by the date of the peak concentration of PCBs in lake trout. This peak occurred between 1974 and 1975 for five to six year-old fish (DeVault *et al.*, 1996). Thus, peak exposure could have occurred as early as 1968 and as late as 1970. This was used as guidance when selecting the year ranges from which the linear functions were chosen. The peak concentration for the intersection of the two functions needed to be near the range of 1968 to 1970. In addition, the simple linear regression model for the onset of contamination had to intersect the x-axis around 1949 when PCBs were first noted in forage fish. The function derived for the onset of PCB loading to the lake is:

$$C_{PCB} = [(-26316.85) + (13.509334 * yr)] \quad (R^2 = 0.865) \tag{1.7.2}$$

where:

C_{PCB} = concentration of PCBs in ng/g

yr = calendar year.

The function derived for the decline of PCB load to the lake is:

$$C_{PCB} = [(15647.899) + (-7.823438 * yr)] \quad (R^2 = 0.897) \tag{1.7.3}$$

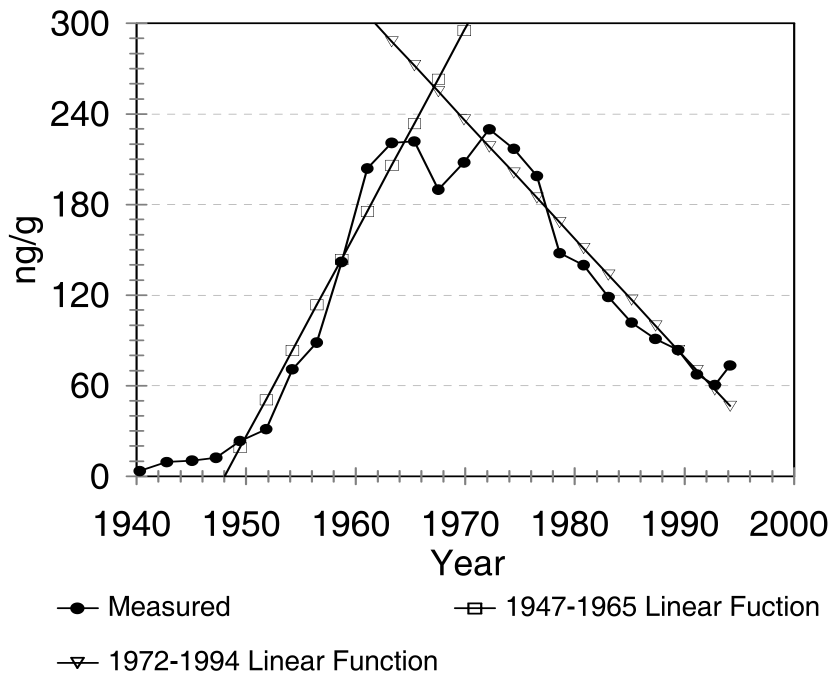

Figure 1.7.2. Fit of concentration functions to observed data for core 15.

The two function lines crossed in roughly 1967. This was considered acceptable and assumed to be the peak load year.

Finally, results from these concentration functions were converted to annual loads. This was done by using mass sedimentation rate information (Rossmann and Edgington, 2000; Rossmann, 2002). The flux of PCBs to the lake can be described as:

$$F_{PCB} = (C_{PCB}) * (MSR) \tag{1.7.4}$$

where

F_{PCB} = flux of PCBs in ng/cm^2/year

MSR = mass sedimentation rate in g/cm^2/year.

This calculated flux was then corrected for physical processes that redistribute sediment within the lake. Sediment focusing is the process by which sediments are moved from one location to another. The process includes sediment resuspension and transport by currents until deposition at another location. The materials that are preferentially resuspended are the fine-grained fraction of sediments. This fraction of the sediments has ^{210}Pb, ^{137}Cs, PCBs, and other contaminants associated with it. Thus sediments at the new deposition site become enriched in these while those at the original resuspension site may become depleted in these. The focusing factor applied was that for ^{210}Pb (Rossmann and Edgington, 2000). The ^{210}Pb focusing factor is defined as:

$$FF_{Pb210} = (A_{210Pb} - AS_{210Pb})/D_{210Pb} \tag{1.7.5}$$

where:

FF_{210Pb} = ^{210}Pb focusing factor

A_{210Pb} = Activity of ^{210}Pb stored in the core for time period year

AS_{210Pb} = Activity of ^{210}Pb supported by radium in the sediment

D_{210Pb} = Decay corrected activity of ^{210}Pb deposited for time period year.

The ^{210}Pb flux from the atmosphere is constant, and the amount stored is calculated from core measurements. The focusing factor corrected PCB flux (FFF_{PCB}) in ng/cm^2/year is calculated using:

$$FFF_{PCB} = F_{PCB} * FF_{210Pb} \tag{1.7.6}$$

This flux is then converted to a load to the lake using the depositional and transitional areas of the lake. The depositional area is defined as the area of the lake with water depths greater than 100 m, the transitional area is defined as the areas of the lake with water depths between 40 and 100 m, and the non-depositional area is defined as the area of the lake with water depths less than 40 m (Figure 1.7.3). Together (excluding Green Bay), the transitional and depositional areas of the lake represent 68.6% of the lake's total area of 58,016 km^2 (Table 1.7.2).

Table 1.7.2. Sedimentary Zones of Lake Michigan

Region of the Lake	Percent of the Lake's Area	Area, km^2
Non-Depositional	24.7	14,334
Transitional	32.8	19,032
Depositional	35.8	20,756
Green Bay	6.7	3,894
Total	100.0	58,016

Flux is converted to load using the equation:

$$L_{PCB} = FFF_{PCB} * (10^{-12}\,kg/ng) * (10^{10}\,cm^2/km^2) * A_{TD} \tag{1.7.7}$$

where:

L_{PCB} = Total load to lake depositional and transitional areas in kg/year

A_{TD} = Total depositional and transitional area of the lake in km^2.

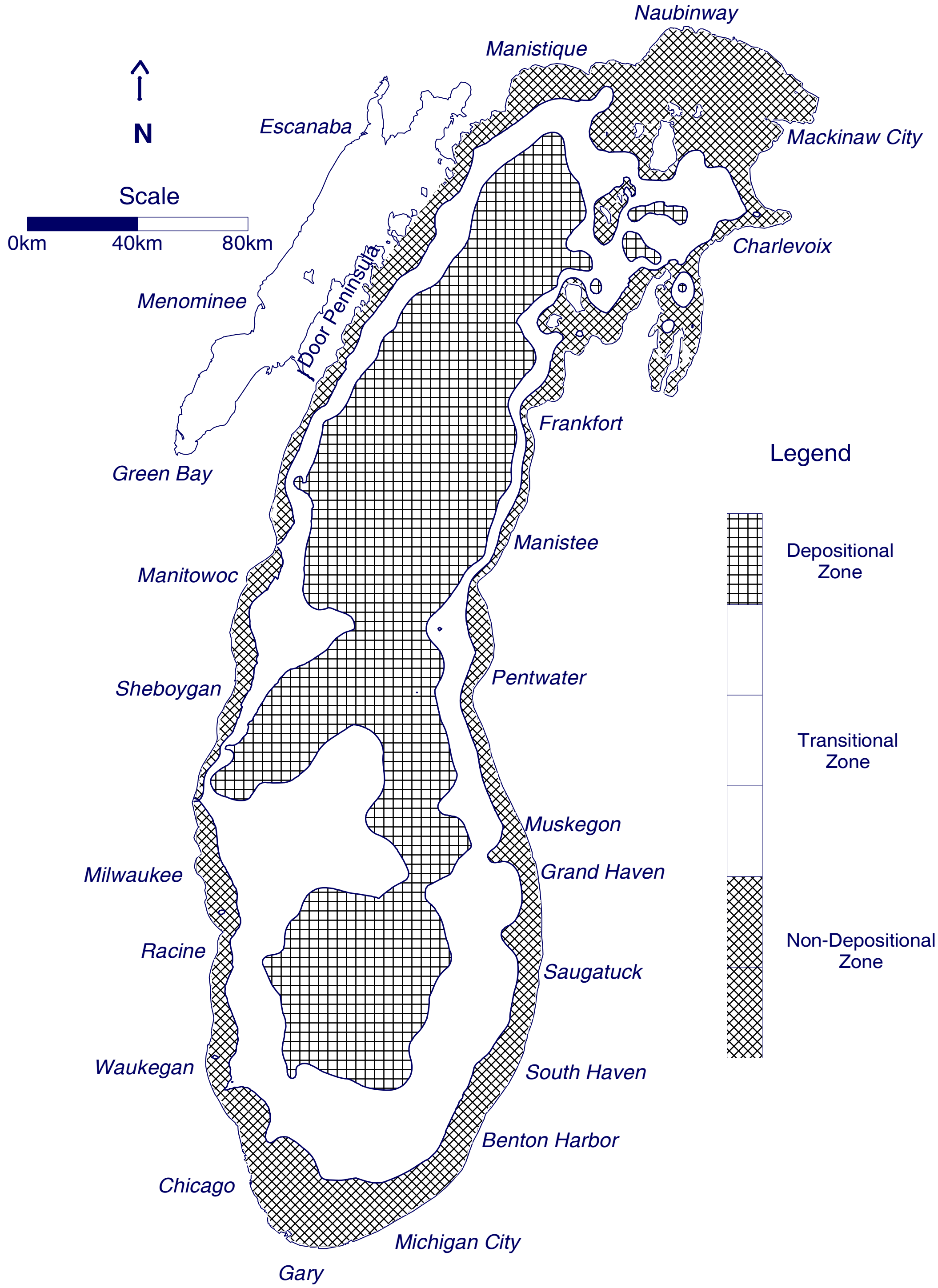

Figure 1.7.3. Lake Michigan non-depositional (0-40 m), transitional (40-100 m), and depositional (> 100 m) zones based on water depth and the depth of wind-wave interaction with sediments.

The remaining terms are unit conversion terms. Loads in the post-peak function were normalized to the 1989 load (2,731 kg/year) because the best linear fit line went through 1989. The result of this function in 1967 of 8,129 kg/year was used to normalize the onset function so that its result in 1967 was also 8,129 kg/year. The resulting load function had a PCB load onset in 1949, a peak load of 8,129 kg/year in 1967, and a 1994 load of 1,504 kg/year (Figure 1.7.4). The 1994 total load was 1.9 times higher than the measured load of 786 kg/year. This was considered within reason because at least one additional loading source was identified since the project. The source is Milwaukee, Wisconsin with an estimated load of 130 kg/year (Wethington and Hornbuckle, 2005). In addition, atmospheric loads did not include the coarse particulate fraction which would contribute an additional load. Franz *et al.* (1998) estimated a particle dry deposition flux of 1,100 kg/year which was considerably higher than previously reported dry deposition fluxes of 16 to 170 kg/year. For the LMMBP, the average particulate PCB flux reported was 120 ng/m^2/month (Miller *et al.*, 2001). This converts to roughly 85 kg/year for the whole lake. Thus the coarse particulate load could be as high as 1,000 kg/year. Therefore, using a load function that results in a 1994 load of 1,504 kg/year seems quite plausible given the uncertainties in the dry deposition fluxes. Finally, it is suspected that other loads, similar to the Milwaukee load, were undetected due to the lack of sampling stations in all metropolitan areas.

1.7.4 Estimated PCB Storage

To provide an estimate of the PCBs stored in Lake Michigan sediment, the three LMMBP core PCB results were manipulated in the same way as described above. This included the application of ^{210}Pb focusing factors to each core so that storage in the entire lake could be estimated. Cores 15, 61, and 86 yielded a lake-wide storage of 209,239, 64,533, and 41,192 kg, respectively. The mean of these is 104,988 kg. This is higher than the 75,000 kg reported by Golden *et al.* (1993). As seen from the three LMMBP cores, storage results are highly variable and location dependent. Application of the above procedure used for estimating storage in the lake's sediments to cores reported in the literature (Golden *et al.*, 1993; Hermanson *et al.*, 1991; Schneider *et al.*, 2001), the mean storage in the main lake is estimated to be 46,466 kg. This is comparable to more recent work by Brian J. Eadie and Patricia Van Hoof (NOAA, Great Lakes Environmental Research Laboratory, Ann Arbor, Michigan, personal communication) based on the LMMBP data which has yielded an estimate of 40,700 kg for the main lake and 60,000 kg for the main lake plus Green Bay.

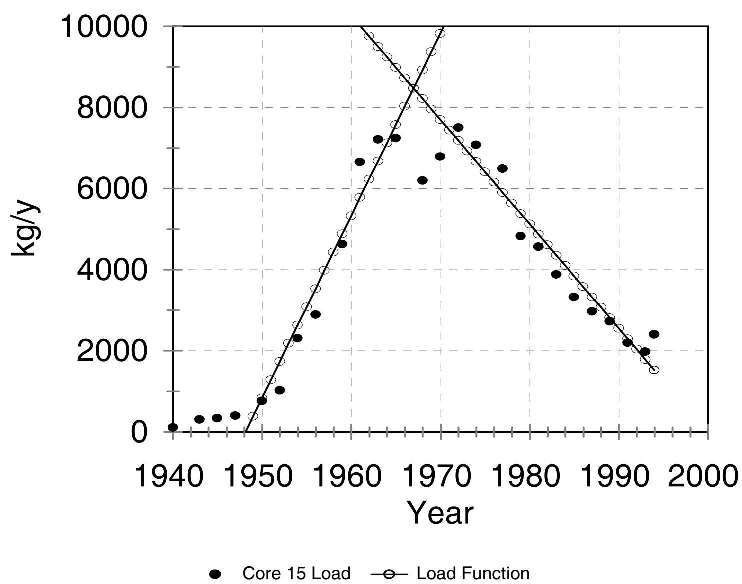

Figure 1.7.4. Comparison of load function to ^{210}Pb focusing factor corrected core 15 loads.

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